

## METHOD FOR THE PRODUCTION OF AN OXIDE CERAMIC SHAPED PART AND A PART PRODUCED BY SUCH METHOD

### CROSS-REFERENCE TO RELATED APPLICATIONS

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This application claims foreign priority benefits under 35 U.S.C. §119 from German patent application Ser. No. 10 2004 004 059.1 filed January 27, 2004.

### TECHNICAL FIELD

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The present invention relates to a method for producing an oxide ceramic shaped part, as well as to an oxide ceramic shaped part.

### BACKGROUND OF THE INVENTION

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Methods for the production of an oxide ceramic shaped part have been known for a long time. For example, it is known from WO 95/35070 to produce a ceramic shaped part. In this approach, the ceramic is infiltrated. The production of an oxide ceramic shaped part of this type is, however, relatively time-consuming; the step alone of the infiltration that is undertaken in connection with this approach, requires, for 20 example, 4 hours.

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Furthermore, it is known from EP-A 1 834 366 to produce a ceramic piece that is produced via the infiltration of a melted matrix material into the hollow space of a blank. A particular particle size with two different size gradations is provided for the infiltration substance. In connection with this approach, a covering material is used 25 that is provided with a soluble salt that must be removed after the infiltration and the solidification step. The disadvantage of this approach is the need for the high process temperature during the shaping and the complicated hardware-intensive production.

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The publication WO 88/02742 discloses the production of a ceramic component 30 having a hardened outer surface. A porous Al<sub>2</sub>O<sub>3</sub> blank is infiltrated with a zirconium

oxide infiltration material so that the finished ceramic work piece comprises a volume portion of 1 to 15 % zirconium oxide and, thus, the so-formed aluminum oxide ceramic is solidified. This process requires several infiltration steps and is suitable if a relatively soft ceramic such as aluminum oxide is to be hardened, while it is to be understood that a zirconium oxide ceramic with a high critical stress intensifying factor cannot be further hardened or strengthened via the addition of zirconium oxide. A ceramic of this type exhibits a strengthening only on its outer surface and, to produce a suitable work piece via this approach, the process steps must frequently be implemented in a serial manner.

Furthermore, DE-A1 198 52 740 discloses the configuration of a cap, or the configuration of other dental pieces, of aluminum oxide ceramic. The pre-sintered shaped part is infiltrated in the heated condition with a glass, which melts upon the introduction of the shaped part into the sintering oven. The infiltration requires, in connection with this approach, a timeframe of approximately 4 hours and a high press temperature. On top of this, the process is decidedly difficult to control and the mechanical properties of the dental piece are correspondingly poor.

Additionally, DE-A1 100 61 630 discloses the production of a full ceramic dental restoration piece comprised of a dental ceramic of zirconium oxide and aluminum oxide, whereby an infiltration with glass in a volume range of 0 to 40 % is undertaken. This approach additionally requires, in connection with the deployment of such a dental restoration piece, the use of a mixture ceramic. A disadvantage of this approach is the reduced securement properties of the ceramic, which has been solidified via the glass phase.

Moreover, EP-A1 1 025 829 discloses the production of a cap of a ceramic material infiltrated with glass. In order to provide the desired translucence, two additional coatings are provided, which are applied onto the cap. In connection with the preparation of the dental restoration pieces, it is, due to aesthetic reasons, critical that the natural dental enamel be simulated, such natural dental enamel having an increased translucence while the dentine has a reduced translucence. In this connection, the coatings 7 and 6 are provided in accordance with the disclosed

approach. In a process of this type, the detailed further working involving the grinding of the infiltrated fixed body into a powder is disadvantageous, but, additionally, the reduced securement property of the ceramic solidified via the glass phase is also disadvantageous.

DE-A1 101 07 451 discloses a process for the production of an oxide ceramic shaped part that is formed from a zirconium or aluminum oxide ceramic via milling with a large CAD/CAM technology system after pre-sintering. Thereafter, the milled blank is sintered under no pressure at 1200 to 1650 °C. The thus produced oxide ceramic phase exhibits a reduced translucence as compared to a high-temperature isostatically pressed ceramic, the mechanical properties are worse than those of a high-temperature pressed ceramic, and such ceramics are difficult to etch.

CH-A5 675 120 discloses zirconium oxide mixture ceramics, which comprise 7 to 12 % by weight  $\text{PiO}_2$  and other grain growth limiting and stabilization suitable additives. These can also comprise 0 to 30 % by weight  $\text{Al}_2\text{O}_3$ . The powder mixture is sintered at a temperature from 1100 to 1300 °C. The disadvantage of this ceramic is that the achievable thickness lies at only 98 % of the theoretical thickness (TD) and, consequently, is less than that of a high-temperature pressed ceramic. The production of a retentive design on the outer surface is, with this ceramic, possible only with difficulty.

Additionally, the publication "Heißisostatisches Pressen" from D. W. Hofer (Heißisostatisches Pressen, in: Technische Keramische Werkstoffe, Fachverlag Deutscher Wirtschaftsdienst, Hrsg. Kriegesmann J., Kap. 3.6.3.0, pp. 1-15. January 1993) discloses that work pieces can be produced via high-temperature pressed processes in which the structures thereof scarcely exhibit any defect locations and the thicknesses of which are nearly those of the theoretically possible values. In order to achieve these properties, however, a pressure of between 30 to 200 MPa is required for the sintering temperatures. Moreover, an inert gas atmosphere follows the step of the pressure treatment. Correspondingly, this technique and the attendant hardware-intensive work require considerable effort and outlay. This process is thus disadvantageous in that it is costly and involves complicated processing technologies

and their attendant high capital and energy costs so that, for example in connection with small enterprises, such as dental laboratories, it is not possible for such enterprises themselves to perform this process.

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## OBJECTS AND SUMMARY OF THE INVENTION

In contrast, the present invention offers a solution to the challenge of providing a method for the production of an oxide ceramic shaped part as well as an oxide ceramic shaped part itself, that is more suitable for the realization of a dental restoration piece and that permits a cost-optimized production with a simultaneously improved aesthetic appearance without degrading the use properties of the thus-produced shaped part and offering, especially, the possibility to produce a retentive design and to ensure the securement of the shaped part on the natural tooth.

Surprisingly, the inventive configuration of an infiltration coating or covering on the relevant regions of the oxide ceramic part permits the realization of an increased securement of the entire oxide ceramic part. Evidently, the covering, or the at least partial covering of the oxide ceramic part with the coating imparted by the infiltration, stabilizes the oxide ceramic shaped part to such an extent that a clearly improved fracture strength approaching  $6.5 \text{ MPa m}^{1/2}$  can be achieved.

In a surprising manner, the inventive solution also leads to an improvement of the aesthetic appearance of a dental restoration piece if the inventive oxide ceramic shaped part is used as the dental restoration piece. The infiltration coating has a higher translucence while the infiltration-free inner region or core of the oxide ceramic has a reduced translucence and, in connection with the realization of a zirconium oxide ceramic, the coating is practically white. This simulates the human tooth in a surprisingly simple manner and is achieved without any need to deploy mixture ceramics, if such is desired.

Due to the possible or optional omission of an additional mixed ceramic, the therewith connected problems also drop out such as the longer process time, the securement problems, and the required coating thickness of the mixture ceramic. In

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contrast, the inventive solution is suitable for the realization of small-scale or closely-spaced members, yet nonetheless aesthetically very attractive, dental restoration pieces. In particular, if the infiltration coating comprises a silicate phase, this can, for example, be etched away with HF and an adhesive binding with other work pieces can be realized.

The inventive solution permits, in a surprisingly simple manner, the achievement of the same securement properties that can be achieved with hot isostatic presses, whereby the time consuming hot-press process can be avoided. The biaxial securement property is, in connection with one embodiment of an oxide ceramic connection part, not less than 800 MPa. The fracture mechanism properties of the pure crystalline oxide ceramic phase are approximately  $6.95 \text{ MPa m}^{\frac{1}{2}}$ , as determined in accordance with the Indenter process and calculations in accordance with Evans & Charles critical tension intensification factors IIC and, in fact, lie comparatively higher than even those of corresponding high-temperature pressed ceramics. It is surprising in this connection that the properties of the hot-pressed materials, even those with predominantly tetragonal zirconium oxide as the crystalline oxide ceramic phase, have been duplicated. Preferably, the thickness of the inventive infiltration coating is between 2 to 30 %; in an advantageous configuration between 5 and 20 %; and, for practical purposes, between approximately 10 to 15 %, each respective selected thickness being a function of the respective largest diameter of the oxide ceramic part.

The coating that at least partially covers the core formed of a non-metallic, inorganic phase is relatively less resistant to acids than the pure crystalline oxide ceramics in the core. The coating can thereby be easily etched. The chemical resistance is, however, not substantially less than that of the core, if the covering coating comprises only micro-crystal zirconium oxide.

Due to the reduced chemical resistance of the coating that at least partially covers the core, a retentive design can be achieved thereat via etching. The depth of this retentive design can be determined via the etching means, its concentration and the application time during the etching process. This depth corresponds in an inventive

manner to, at the most, the thickness of the covering coating, as the core is substantially more resistant to chemical attacks than the covering coating.

In the realization of the inventive process, a pre-sintering to achieve 50 % of the theoretical thickness in atmospheric air is undertaken at no pressure following the pressing of the oxide ceramic blank. In the realization of the inventive process, a powder or a powder mixture is provided as the outlet material, which is formed out of the corresponding oxide ceramic or mixture ceramic. The powder is preferably in the form of a granulate and is mixed with a binding material. Preferably, the binding material can be comprised of ethylene wax material, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl acetate, polyvinyl butyral, or cellulose.

The pre-sintering temperature amounts to clearly less than the sintering temperature and can lie, for example, between 600 and 1300 °C and, preferably, between 1000 and 1200 °C.

To achieve the inventive solution, it is advantageous to evacuate the partially sintered part. In this connection, in accordance with the invention, less than 50 mbar, such as, for example, 20 mbar, is preferred. The low pressure is applied, for example, for 1 minute up to 4 hours such that a pressure equalization in the sense of the formation of a vacuum in the interior of the partially sintered oxide ceramic shaped part is formed. In connection with this evacuation, the gases are removed from the porous, partially sintered in-process part body. During this time, the inventive sol. to be deployed for preparing the further materials that are to be formed, is mixed. In a conventional manner, the formation of these further materials is undertaken following the evacuation in a low pressure atmosphere.

It is particularly advantageous, in connection with the inventive method, that the penetration of a precursor of a non-metallic, inorganic phase has shown its worth, such precursor comprising, for example, a precursor of a vitreous-amorphous phase and a solvent.

In accordance with the present invention, it is particularly advantageous if the infiltration material is available as a sol. and is further reacted into a gel. These are preferably precursor products of a glass or ceramic material. Via the low pressure, the

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mixed sol. is suctioned into the low pressure chamber and there follows a penetration over an inventive, decidedly short time, such as, for example, preferably, 1 minute. In this manner, there is achieved an infiltration coating with the desired coating thickness, which permits the setting or adjustment thereof via the infiltration time, the viscosity of the solution, but as well, the porosity of the partially-sintered ceramic part.

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Surprisingly, the formation of the infiltration coating in a simple manner permits the realization of a decidedly uniform coating. Due to the short infiltration time, the infiltration fluid only has time for the outer surface of the in-process part body to be covered. Via aeration of the low pressure chamber, the infiltration material is practically suctioned in. It is to be understood that the viscosity of the preferably gel-formed infiltration material substantially influences the penetration depth. A reduced viscosity produces, due to the reason of the capillary working of the pores of the in-process part body, a large coating thickness of the infiltration coating, while a high viscosity reduces the penetration depth. Preferably, the coating thickness amounts to approximately 0.5 mm. In a modified embodiment, the coating thickness of the infiltration coating is approximately 1.5 mm, which corresponds to the coating thickness of the dental enamel, but this coating thickness can be adjusted to more or less, as well.

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Immediately after this step, there follows an aeration of the low pressure chamber and the solidification of the applied solution into a gel is undertaken via heating at the pre-selected sintering temperature in an ambient atmosphere. The sintering temperature is, for example, 1300 to 1550 °C and the sintering follows under an ambient pressure at an ambient atmosphere. Via the inventive process, the sintering properties of the pure crystalline oxide ceramic phase are improved while, via a covering coating formed from a non-metallic, inorganic phase of the previously evacuated, partially-sintered shaped part, the penetration of gases into the porous structure of the partially-sintered part is prevented, whereby a complete dense sintering of the ceramic is achieved.

The inventive oxide ceramic shaped part can be pre-pressed in a desired form. It is also, however, possible to undertake a milling or another type of cutting or machining in order to produce a shaped part from the ceramic in-process part body and, in fact, to accomplish such, either after the pre-sintering or after the sintering.

5 With respect to such an undertaking after the pre-sintering, the advantage is gained that the shaping is possible in a relatively easy manner in that the final hardness has not yet been reached. In contrast, in connection with such an undertaking after the sintering, a very hard work piece such as a diamond-cutting disc must be used whereby, to be sure, the shape integrity is not degraded by a further shrinking process.

10 In accordance with the present invention, an oxide ceramic shaped part with a theoretical thickness of 99.9 % is produced via, for example, sintering at 1480 °C, whereby it is advantageous that, during the sintering in an ambient atmosphere, the shaped part is worked so that the shrinkage factor is less than that of a high-temperature isostatic press process.

15 The inventive process permits the preparation of a substantially tetragonal phase with reduced cubical phase components, provided that a sintering temperature of 1500 °C is not exceeded. In accordance with the present invention, in a surprising manner, a translucence profile is realized that heretofore could only be realized via a hot-press process. Additionally, in contrast to a hot-press ceramic, the advantage is obtained  
20 that an adhesion via etching on the infiltration coating is possible without further effort.

25 The present invention is particularly advantageous in connection with zirconium oxide ceramic or mixture ceramics having a high zirconium oxide portion, whereby, as well, suitable doping - such as with yttrium - and mixing-in can be advantageous. In connection with such hard ceramics, the bending strength in the core is high, the fracture strength, in contrast, is particularly good in the infiltration coating, which is formed from the crystalline oxide ceramic phase and the infiltration phase that penetrates the crystalline oxide ceramic phase – also called infiltration.

30 The thus-produced inventive oxide ceramic composite shaped part comprises, consequently, in its pure crystalline oxide ceramic core, the optical and mechanical

properties which even equal the values of those properties in the high-temperature isostatic pressed materials. The properties of the pure crystalline oxide ceramic phase are, evidently, realized by the reason of the thickness of the structure.

In one embodiment, following the finish sintering, there is effected, to inventively produce an oxide ceramic composite shaped part, a process in which a material reduction working occurs that is, preferably, performed by CAD/CAM technology. In this connection, the covering coating is completely or partially reduced away and the translucent core comes to the outer surface. In this manner, the final shaping of the oxide ceramic composite shaped part can subsequently occur. If the covering coating remains in a partially covering manner on the outer surface, this can be removed in a following step via etching.

A retentive design can be maintained in the regions where the outer coating still remains. At the same time, a thick, translucent structure appears on those portions of the outer surface at which the coating has been removed. In this manner, there is produced, in a surprisingly simple manner, an aesthetic appearance that corresponds to that produced in connection with comparable hot isostatic press work pieces. Due to the high density of the structure, a high light transmission capability (translucence) is achieved that corresponds to that of hot isostatic pressed ceramic.

To configure a dental restoration piece, a single coat mixture is subsequently applied in order to produce an even more improved aesthetic appearance. In the regions in which a retentive design was produced, the use of suitable desired adhesive systems is possible. Preferably, an adhesive system is deployed. In accordance with the present invention, an adhesive securement is possible in a surprisingly simple manner which is not possible with respect to corresponding hot isostatic pressed work pieces. In connection with the securement materials, chemical, light-hardenable, or dual hardenable material are preferred. Cementing materials are, for example, zinc phosphates. The inventive oxide ceramic composite shaped part offers, in this manner, an improved adhesive procurement possibility with the same aesthetic appearance as hot isostatic pressed, comparable materials. Moreover, the sintering process is

substantially simpler and is, consequently, in contrast to the hot isostatic press process, considerably more cost favorable.

5       The inventive solution permits a plurality of oxide ceramic parts to be produced. In this connection, dental restoration pieces are produced such as inlays, onlays, crowns, partial crowns, veneers, facets, bridges, caps, brackets and abutments, but also alluvial materials, and alluvial material components and frameworks.

10      Also, it is basically possible to exploit the advantages of the inventive process in connection with other deployed ceramic pieces such as, for example, the preparation of synthetic joints, whereby the outer surface infiltration coating offers favorable properties in view of the reduced abrasion with, at the same time, good hardness and a glass-hard outer surface; however, surgical implants or components thereof are equally amenable to such preparation. Also, endodontic parts such as root posts can be produced by the inventive process whereby the good adhesion on other parts can be exploited.

15      The length of time of the production of an inventive ceramic blank is strongly dependent upon the length of time required for the desiccation - that is, the creation of the low pressure environment. The preparation of the infiltration material requires, in connection with one advantageous embodiment of the invention, a not inconsiderable mixing time and standing time. The determination of the time frame can, however, be favorably influenced by the mixing of the infiltration material already before the 20 process has begun - that is, for example, while the blank is pressed or, at the latest, during the pre-sintering, so that this mixing time does not add onto the cycle time for the preparation of a finished oxide ceramic part.

25      The pure infiltration time can, for example, amount to 1 or 2 minutes and can last, in any event, typically less than 10 minutes while the finish infiltration occurs in accordance with the respective selected temperature curve of, for example, 30 to 60 minutes.

30      Further advantages, details, and features are described in the hereinafter following descriptions of several embodiments of the present invention with reference to the drawings.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic perspective view of an arrangement for performing the inventive infiltration method for preparing an infiltration coating on an oxide ceramic part;

Figure 2 is a graphical view of the infiltration coating thickness versus the infiltration time;

Figure 3 is a schematic perspective view of a sintering oven for use in connection with the inventive infiltration method for preparing an infiltration coating on an oxide ceramic part;

Figure 4 is a flow chart of the steps of one implementation of the method of the present invention; and

Figure 5 is a flow chart of the steps of another implementation of the method of the present invention.

## DETAILED DESCRIPTION

Figure 1 schematically illustrates an arrangement for performing the inventive infiltration method for preparing an infiltration coating on an oxide ceramic part. The blank 10, which subsequently forms the oxide ceramic part, is pre-sintered and is disposed in a beaker 12. The beaker 12 is disposed in a desiccator 14 on whose cover a drip funnel 16 is mounted.

Moreover, the desiccator comprises, in a conventional manner, a low-pressure connection hose 18 that is connected with a low-pressure pump. In a conventional manner, the polished sealing edge 20 of the desiccator closes upon the creation of a low pressure environment in the desiccator and can be opened after the venting of the desiccator. The drip funnel does not have a pressure compensation but is, however, provided with a stopcock 22 that permits a fine adjustment of the drip rate.

The infiltration is effected in a manner such that a prepared brine 22 is introduced as the infiltration material into the drip funnel 16, after which the desiccator 14 is brought to a low pressure of, for example,  $20 \times 10^{-3}$  bar.

As soon as the desired pressure is reached, the stopcock 22 is opened in the desired manner. The beaker 12 is filled up to a maximum fill level 24 with infiltration material that later penetrates into the blank 10. The penetration is effected principally from the topside and the side walls while the underside, which is disposed on the beaker 12, is somewhat less strongly infiltrated.

Although Figure 1 illustrates a cylindrical blank 10, it is to be understood that, in practice, predetermined shaped parts are produced which are disposed on the base of the beaker 12 and are wetted with infiltration material. After an infiltration time of 1 minute, an infiltration coating in a thickness of 0.3 to 0.6 mm has already been formed therefrom.

Figure 2 is a graphical illustration of the infiltration coating depth as a function of the infiltration time. In accordance with the present invention, it is advantageous that the coating thickness in many regions can be accommodated to the requirements. Thus, very fine-sectioned and thin oxide ceramic parts with a decidedly low infiltration coating thickness which, however, offers a certain translucence but, as well, offers a good securing of the core, can also be worked.

It is advantageous, for example, in connection with an infiltration depth of 1 mm or somewhat less, to simulate the natural tooth enamel. The preferred region for the infiltration depth is, however, greater than 0.4 mm.

Figure 3 is a schematic illustration of a sintering oven 26. The sintering oven comprises a plurality of heating elements 28 and a crucible 30 that receives therein the blank 10 after infiltration. Preferably, in a conventional manner, the crucible is provided with a powder coating and there follows a heating or a finish infiltration of the blank 10 to form the oxide ceramic part within less than 1 hour, including the heating up time.

In the hereinafter following descriptions, various embodiments are described in more individual detail.

## Example 1

A dry press granulate of ZrO<sub>2</sub> powder is used for the raw material for the blank 10. It is doped with yttrium and comprises other components such as Al<sub>2</sub>O<sub>3</sub>. The dry press granulates can be, for example, those available from the TOSOH company with the commercial designation TZ-3YB and TZ-8YB and having a primary crystal size of 280 – 400 nm and a granulate size of 50 µm but, as well, can be the granulate available under the commercial designation of TZ-3Y20AB that is characterized by the addition thereto of 20% Al<sub>2</sub>O<sub>3</sub> and that otherwise corresponds to the other granulates.

In accordance with the following table, powdery oxidized raw materials in predetermined mole portions are added to the zirconium oxide ceramics.

Raw Material		TZ3YB	TZ3YB	TZ3YB	TZ3YB	TZ8YB	TZ8YB	TZ8YB
Oxide								
CeO <sub>2</sub>	/mol-%	2.5	5	8	10	15	--	--
Er <sub>2</sub> O <sub>3</sub>		2.5	5	---	---	---	---	---
CeO <sub>2</sub>	+ /mol - %	3 + 3	---	---	---	---	---	---
Sc <sub>2</sub> O <sub>3</sub>	/mol-%	3	---	---	---	---	---	---
TiO <sub>2</sub>	/mol-%	10	15	---	---	---	10	15

In this inventive experiment, cylindrical press forms with inner diameters of 12 and 16 mm were used. The pressing of the blank 10 was effected in a conventional manner with pressures of 500, 600 to 1100 bar, whereby the press pressure was reached in 5 seconds, then held for 15 seconds at the maximum pressure, and then reduced within a further 5 seconds.

Thereafter, there followed the pre-solidification step during which, at the same time, the release was effected and this is shown in the following table, which shows the serially following time segments of the pre-sintering process with the slopes indicated in the left hand column.

	Slope	${}^{\circ}\text{C}_{\text{Rn}}$ / ${}^{\circ}\text{C}$	${}^{\circ}\text{C}_{\text{Rn} + 1}$ / ${}^{\circ}\text{C}$	Heat rate / K min $^{-1}$	K h $^{-1}$	Time /min	Time /h
5	1	0	320	2.5	150	128	2:08
	2	320	470	1	50	150	2:30
	3	470	1100	2.5	150	252	4:12
	4	1100	1100	0	0	20	0:30
						560	9:20

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The powder comprises a binder in the form of a press assistance material and, via the dry pressing in the following bond release, the introduced binding material was burnt out and the blank was thus formed with a porous structure. Thereafter, the pre-sintering was performed. After the pre-sintering, a part with 50 % thickness depth (TD) was achieved.

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The evacuation of the blank 10 was performed in the desiccator 14 with a finish pressure of approximately 20 mbar. Due to the comparatively long evacuation time, which, in any event, amounted to more than 1 hour, the gas enclosed in the porous blank was substantially removed.

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Infiltration material based upon tetraethoxysilane/tetraethylorthosilicate (TEOS) was used. TEOS was, together with water with a catalyst of aluminum nitrate nonhydrate( $\text{Al}(\text{NO}_3)_3$ ) x 9 H<sub>2</sub>O), mixed with a sol. As a function of the mixing time and the subsequent standing time, the sol. reacted slowly into a gel and condensed into a glass-similar structure. Cerium nitratheydrate was also introduced to the actual catalyst.

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It was attempted to prepare the infiltration material so that, after the infiltration into the infiltration coating, a firm gel was quickly formed which converted after the sintering into a silica glass phase. The infiltration coating was comprised, in accordance with the invention, principally of tetragonal crystalline zirconium oxide phases as well as an amorphous glass phases, substantially from condensed TEOS, while the core of the inventive oxide ceramic piece was substantially comprised of zirconium oxide with the previously noted doping, which was, in any event, predominantly in tetragonal phase.

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The attempts with various mixing relationships of TEOS,  $(\text{Al}(\text{NO}_3)_3) \times 9 \text{ H}_2\text{O}$  as well as  $\text{Ce}(\text{NO}_3)_3 \times 9 \text{ H}_2\text{O}$  revealed the tendency, in connection with longer mixing times, that the solidification time - that is, the standing time until solidification - decreased. The sums or totals of the times amounted to typically 6 to 7 hours, whereby the omission of the cerium nitratehydrate in certain mixing relationships was able to produce solidification after a mixing time of 3 hours.

The prepared infiltration material was then introduced into the drip funnel and the stopcock 22 was opened and, in fact, was opened to the extent that the blank was, in any event, fully covered following the introduction of the sol., but not so far as to permit an excess of infiltration material to flow through the drip funnel, as such would have delayed the venting of the desiccator.

The venting followed the complete opening of the stopcock, after which the drip funnel 16 became empty.

The infiltration material that had been introduced through the desiccator and thereafter placed under low pressure initially foamed, whereby the low pressure was maintained.

As can be seen in Figure 2, the infiltration depth is dependent not only upon the viscosity of the introduced infiltration material but, as well, is, in particular, dependent upon the mixing time and the standing alone time of the infiltration material (the difference between ZIO15 and ZIO16b).

It is contemplated that the time for the process is to be selected such that the solidification of the infiltration material occurs after or during the infiltration. It is not critical if the infiltration material has already solidified, whereby, as well, in connection with fluid infiltration material, a thickening of the coating is anticipated in that, as well, a fluid infiltration material closes the pores of the blank 10.

Infiltration material remainders on the ceramic blank were then removed easily with a towel and there followed an air-drying step, whereby the inventive examples were subjected to an air-drying of 1 to 2 hours.

The finished sintering followed in the same sintering oven which had been deployed for the pre-sintering and the sintering curve is shown in the following table in 3 time segments.

5	Slope	$^{\circ}\text{C}_{\text{R}_n}$	$^{\circ}\text{C}_{\text{R}_n + 1}$	Heat rate		Time /min	Time /h
	/ °C	/ °C	/ K min <sup>-1</sup>	K h <sup>-1</sup>			
10	1	0	1000	5	300	200	3:20
	2	1000	1480	2.5	1450	192	3:12
	3	1480	1480	0	0	30	0:30
						422	7:02

In this connection, the blank was sealed in a quartz frit - or  $\text{Al}_2\text{O}_3$  - powder bed in an aluminum oxide crucible.

15 The results showed that the sintered blank comprises an infiltration coating thickness which, in dependence upon the infiltration time, is of varying thickness.

There was also obtained a good translucence of the oxide ceramic part and, in the interior of the blank, a tetragonal phase with an average crystal size of 0.4 to 0.5 micrometers was present.

20 The smallest achieved infiltration depth, in connection with the above-noted infiltrate based upon TEOS, amounted to approximately 180 micrometers.

### Example 2

25 In a modified example, in lieu of TEOS, a zirconium (IV) propylate ( $\text{Zr(IV)Pr}$ ) was deployed. This zirconium (IV) propylate was used in lieu of TEOS and, when subjected to atmospheric pressure with water, was driven as zirconium oxide particles out of the pores of the blank. Also, in this connection, the pores could be closed, whereby the crystalline particles in the pores precipitate out, which corresponds to the actual base material. The thus achieved minimal coating thickness of the infiltration coating amounted to approximately 50 micrometers.

## Example 3

In total, the inventive process produced an oxide ceramic composite shaped part with high fracture strength, whereby the translucence properties corresponded to those of zirconium oxide ceramic (TZP) which are deployed in connection with the high-temperature isostatic press process.

Sample	Ptr /bar	t <sub>inf.</sub> /min	V <sub>Br</sub> / C	Density (in the core) /g cm <sup>-3</sup>	Light Transmission Capability (comparison) %	HV 10 /MPa	K <sub>IC</sub> -Value (Evans & Charles) /MPa m <sup>1/2</sup>
A1235	1000	1	1480	6.08	70.7	---	---
A1237	1000	5	1480	6.10	75.0	---	---
A1240	1000	2	1480	---	---	13220	6.95
A1245	900	1	1480	---	---	13055	6.55
A1246	900	1	1480	6.08	72.2	---	---
Mexoxit Bio-HIP ZeO <sub>2</sub> (comparison measurement)	unknown	unknown	unknown	6.07	70.3	12850	6.65
Denzir DO HIP-ZrO <sub>2</sub> (comparison measurement)	unknown	unknown	unknown	6.10	76.4	12830	6.70
A1253	900	Not infiltrated	1480	5.88	56.4	---	---
A1254	900	Not infiltrated	1480	---	---	12900	6.17

As can be seen in the foregoing, it is clear that the conventional sintered

examples not produced in accordance with the present invention exhibit considerably worse properties with respect to light transmission capability and fracture strength.

## Example 4

Additionally, several attempts were made in connection with the inventive process to effect the etching with HF and an etching retentive design was produced in correspondence with the length of time. Etching attempts were undertaken by which the outer coating was completely etched away and only the inner oxide ceramic core remained. By covering the infiltration coating with wax or a polymer coating, it is also possible that selected locations can remain unetched.

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## Example 5

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In correspondence with the above noted type and manner of shaped part handling, a cylindrical part with a diameter of 12 mm and a height of 25 mm was produced via pressing of a granulate obtained from the Tosoh company (TZ 3YB) and subsequent pre-sintering at 1100 °C. To perform thereafter a shaping of the part, a CEREC Inlab milling machine available from the Sirona Company was deployed, whereupon the thus-produced shaped part was a crown having excess material. The excess material had to be removed so that, following the shrinking which occurs in connection with the sintering and the partial etching away of the covering coating, an optimal size accommodation or fitment to the model frame was be produced. In accordance with the present invention, the thus obtained partially sintered and milled part was then provided with a covering coating in a vacuum-configured environment, whereby the applied material generally penetrated into the outer surface of the porous partially sintered part. During the subsequent sintering process in ambient air at ambient pressure, a finished sintered crown was produced that, following partial etching away of the covering coating, exhibited, on the one hand, a retentive design and, on the other hand, a good size accommodation or fitment to the model frame.

Figures 4 and 5 each show respective illustrations of the results of the process steps in various configurations of the inventive method. The thus-depicted configurations of the inventive method differ from one another with respect to the

timing of the machining or trimming step: with respect to the configuration "Technology II" depicted in Figure 5, the machining or trimming step is performed before the infiltration step while, with respect to the configuration "Technology I" depicted in Figure 4, the trimming step is performed after the finish sintering step.

5 The respective configuration of the inventive method shown in Figure 4 requires greater tooling efforts in view of the high degree of securement of the substantially completely finished sintered dental restoration piece; however, this configuration of the inventive method offers a somewhat greater degree of precision.

In all, the demonstrations conducted with respect to the inventive method resulted in an oxide ceramic part having a high fracture strength of 6.95 MPa m<sup>1/2</sup>, whereby the translucence properties were correspondingly satisfactory and corresponded to those of oxide ceramic parts that have been produced by high-temperature isostatic press processes.

The present invention is, of course, in no way restricted to the specific disclosure of the specification and drawings, but also encompasses any modifications within the scope of the appended claims. While a preferred form of this invention has been described above and shown in the accompanying drawings, it should be understood that applicant does not intend to be limited to the particular details described above and illustrated in the accompanying drawings, but intends to be limited only to the scope of the invention as defined by the following claims. In this regard, the term "means for" as used in the claims is intended to include not only the designs illustrated in the drawings of this application and the equivalent designs discussed in the text, but it is also intended to cover other equivalents now known to those skilled in the art, or those equivalents which may become known to those skilled in the art in the future.

25 What is claimed is: